

THERMAL TREATMENT OF FUNCTIONALIZED CARBON NANOTUBES IN SOLUTION TO EFFECT THEIR DEFUNCTIONALIZATION

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CROSS REFERENCE TO RELATED APPLICATIONS

[0002] This Application claims priority to United States Provisional Patent Application Serial No. 60/516,392, filed October 31, 2003.

FIELD OF THE INVENTION

[0003] The present invention relates generally to carbon nanotube materials. More specifically, the invention relates to methods of defunctionalizing previously functionalized carbon nanotubes.

BACKGROUND OF THE INVENTION

[0004] Carbon nanotubes (CNTs), comprising multiple concentric shells and termed multi-wall carbon nanotubes (MWNTs), were discovered by Iijima in 1991 [Iijima, *Nature* **1991**, 354, 56-58]. Subsequent to this discovery, single-wall carbon nanotubes (SWNTs), comprising single graphene sheets rolled up on themselves to form cylindrical tubes with nanoscale diameters, were synthesized in an arc-discharge process using carbon electrodes doped with transition metals [Iijima *et al.*, *Nature* **1993**, 363, 603-605; and Bethune *et al.*, *Nature* **1993**, 363, 605-607]. These carbon nanotubes (especially SWNTs) possess unique mechanical, electrical, thermal and optical properties, and such properties make them attractive for a wide variety of applications. See Baughman *et al.*, *Science*, **2002**, 297, 787-792.

[0005] Methods of making CNTs include the following techniques: arc discharge [Ebbesen, *Annu. Rev. Mater. Sci.* **1994**, 24, 235-264]; laser oven [Thess *et al.*,

Science **1996**, 273, 483-487]; flame synthesis [Vander Wal *et al.*, *Chem. Phys. Lett.* **2001**, 349, 178-184]; and chemical vapor deposition [United States Patent No. 5,374,415], wherein a supported [Hafner *et al.*, *Chem. Phys. Lett.* **1998**, 296, 195-202] or an unsupported [Cheng *et al.*, *Chem. Phys. Lett.* **1998**, 289, 602-610; Nikolaev *et al.*, *Chem. Phys. Lett.* **1999**, 313, 91-97] metal catalyst may also be used.

[0006] Techniques of chemically functionalizing CNTs have greatly facilitated the ability to manipulate these materials, particularly for SWNTs which tend to assemble into rope-like aggregates [Thess *et al.*, *Science*, **1996**, 273, 483-487]. Such chemical functionalization of CNTs is generally divided into two types: tube end functionalization [see, *e.g.*, Liu *et al.*, *Science*, **1998**, 280, 1253-1256; Chen *et al.*, *Science*, **1998**, 282, 95-98], and sidewall functionalization [see, *e.g.*, PCT publication WO 02/060812 by Tour *et al.*; Khabashesku *et al.*, *Acc. Chem. Res.*, **2002**, 35, 1087-1095; and Holzinger *et al.*, *Angew. Chem. Int. Ed.*, **2001**, 40, 4002-4005], and can serve to facilitate the debundling and dissolution of such CNTs in various solvents. Scalable chemical strategies have been, and are being, developed to scale up such chemical manipulation [Ying *et al.*, *Org. Letters*, **2003**, 5, 1471-1473, Bahr *et al.*, *J. Am. Chem. Soc.*, **2001**, 123, 6536-6542; and Kamaras *et al.*, *Science*, **2003**, 301, 1501].

[0007] Carbon nanotube chemistry has been described using a pyramidization angle formalism [Niyogi *et al.*, *Acc. of Chem. Res.*, **2002**, 35, 1105-1113]. Here, chemical reactivity and kinetic selectivity are related to the extent of *s* character due to the curvature-induced strain of the sp^2 -hybridized graphene sheet. Because strain energy per carbon is inversely related to nanotube diameter, this model predicts smaller diameter nanotubes to be the most reactive, with the enthalpy of reaction decreasing as the curvature becomes infinite. While this behavior is most commonly the case, the role of the electronic structure of the nanotubes in determining their reactivity is increasingly important—especially when desiring selectivity among a population of similar-diameter CNTs (such as is often the case with SWNT product).

[0008] The diameter and chirality of individual CNTs are described by integers "*n*" and "*m*," where (*n,m*) is a vector along a graphene sheet which is conceptually rolled up to form a tube. When $|n-m| = 3q$, where *q* is an integer, the CNT is a semi-metal (bandgaps on the order of milli eV). When $n-m = 0$, the CNT is a true metal and

referred to as an "armchair" nanotube. All other combinations of n-m are semiconducting CNTs with bandgaps typically in the range of 0.3 to 1.0 eV. See O'Connell *et al.*, *Science*, **2002**, 297, 593. CNT "type," as used herein, refers to such electronic types described by the (n,m) vector (*i.e.*, metallic, semi-metallic, and semiconducting).

[0009] All known preparative methods lead to polydisperse materials of semiconducting, semimetallic, and metallic electronic types. See M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996; Bronikowski *et al.*, *Journal of Vacuum Science & Technology* **2001**, 19, 1800-1805; R. Saito, G. Dresselhaus, M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998. As such, a primary hurdle to the widespread application of CNTs, and SWNTs in particular, is their manipulation according to electronic structure [Avouris, *Acc. Chem. Res.* **2002**, 35, 1026-1034]. Recently, however, methods to selectively functionalize CNTs based on their electronic structure (*i.e.*, electronic type) have been reported [Strano *et al.*, *Science*, **2003**, 301, 1519-1522; commonly assigned co-pending International Patent Application PCT/US04/24507, filed July 29, 2004]. In such reports, metallic CNTs are seen to react preferentially with diazonium species, permitting a separation or fractionation of metallic (including semimetallic) and semiconducting CNTs via partial functionalization of a mixture of metallic and semiconducting CNTs. For a detailed discussion of CNT types and their optical identification, see Bachilo *et al.*, *Science*, **2002**, 298, 2361-2366.

[0010] Regeneration of the pristine-like nanotube structure becomes of paramount importance if covalent functionalization is used as a handle for separation or for controlled manipulation of material, particularly when the original extended π -electron-derived optical or electronic properties are required for the ultimate desired function. It has been shown that functionalized material treated thermally, in the dry state, in an inert atmosphere, defunctionalizes to regenerate the pristine-like SWNT structure [Dyke *et al.*, *J. Am. Chem. Soc.* **2003**, 125, 1156-1157; Dyke *et al.*, *Nano Lett.* **2003**, 3, 1215-1218; Bahr *et al.*, *J. Am. Chem. Soc.* **2001**, 123, 6536-6542; and Bahr *et al.*, *Chem. Mater.* **2001**, 13, 3823-3824]. However, material treated thermally in the dry state is intractable; it can not be resuspended in organic solvent even with extended sonication. Two possible mechanisms exist for explaining the loss of

solubility. First, covalent cross-linking of multiple nanotubes might ensue during thermolysis via radical reactions. Secondly, as the material is annealed, defects are moved to the ends of the nanotube thereby providing bundled material that is energetically difficult to unbundle. This second possibility could be the reason that even thermally treated pristine (unreacted) material is difficult or impossible to solublize. Note that nanotubes have a reported van der Waals attraction of 0.5 eV per nanometer of tube–tube contact [O’Connell *et al.*, *Chem. Phys. Lett.* **2001**, 342, 265-271; and Thess *et al.*, *Science* **1996**, 273, 483-487].

[0011] In light of the above-described advances in the chemical functionalization of CNTs, and the disadvantages of current thermal defunctionalization methods, a better method of regenerating pristine carbon nanotubes from functionalized carbon nanotubes is clearly needed.

BRIEF DESCRIPTION OF THE INVENTION

[0012] The present invention is directed towards methods of thermally defunctionalizing functionalized (derivatized) carbon nanotubes (CNTs) in solution or while suspended in a liquid medium. Such defunctionalization largely comprises the removal of sidewall functionality from the CNTs, but can also serve to remove functionality from the CNT ends. Such methods allow for the resuspension of such defunctionalized CNTs in various solvents and permit the defunctionalization of functionalized CNTs that would normally decompose (or partially decompose) upon thermal treatment. Such methods of defunctionalization can typically lead to defunctionalized CNTs that are essentially pristine (or nearly pristine), and which, in contrast to prior art methods of thermal defunctionalization, can be easily resuspended in a variety of solvents.

[0013] The methods of the present invention generally comprise the steps of: (a) suspending/dissolving a quantity of functionalized CNTs in a solvent to form a suspension/solution of functionalized CNTs; and (b) heating said suspension/solution to a temperature that will thermally defunctionalize the functionalized CNTs yielding a defunctionalized product. Temperatures exceeding the atmospheric pressure boiling point of the solvent are easily achieved by sealing the mixture in a closed pressure vessel.

[0014] The methods of the present invention are flexible in that they work with a variety of different kinds of functionalized CNTs, and they can employ a variety of different solvents. In some embodiments, the functionalized CNTs have been partially and/or selectively functionalized (e.g., by electronic type). In some embodiments, the solvent selection is directed by the kinds of functionalized CNTs being defunctionalized.

[0015] In some embodiments, the defunctionalization is used to render a partially defunctionalized product. By carrying out the defunctionalization in solution, the defunctionalization can be homogeneous. Such partial defunctionalization can lead to functionalized CNTs with stoichiometries that might otherwise be unattainable with direct functionalization methods.

[0016] In some embodiments, one or more analytical techniques are used to evaluate the defunctionalized product. Such techniques can be used to determine the extent of defunctionalization and the extent to which the defunctionalized CNTs have been returned to their pristine (original) state.

[0017] While many of the exemplary embodiments described herein utilize single-wall carbon nanotubes (SWNTs), it should be understood that such methods are generally applicable to all functionalized carbon nanotubes.

[0018] The foregoing has outlined rather broadly the features of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:

[0020] FIGURE 1 illustrates two reaction schemes by which SWNTs can be functionalized by diazonium species, where in reaction 1 the diazonium species is generated *in situ* under solvent free conditions, and where in reaction 2 the diazonium species is added directly to a surfactant-aided suspension of SWNTs;

[0021] FIGURE 2 depicts a thermogravimetric analysis (TGA) plot of the thermal defunctionalization of heavily functionalized (4-chlorophenyl) SWNTs in the dry state;

[0022] FIGURES 3 A-E depict Raman spectra (taken with 633 nm excitation) of (A) pristine (unreacted) SWNTs, (B) heavily functionalized SWNTs containing 4-chlorophenyl addends by treatment of micelle-coated SWNTs with 4-chlorobenzenediazonium tetrafluoroborate and corresponding to the material used for the TGA in FIGURE 2, (C) the same material as in 3B, but after neat thermal treatment at 10°C/min to 650°C in Ar, (D) the same material as in 3B, but after neat thermal treatment at 10°C/min to 450°C and holding at 450°C for 2 hours, and (E) the same material as in 3B, but after thermal defunctionalization in ortho-dichlorobenzene (ODCB) at 450°C for 3 hours; and

[0023] FIGURE 4 illustrates the thermolysis of 4-*tert*-butylphenyl-functionalized SWNTs (prepared by the SDS-coated SWNT/H₂O protocol) in ODCB (solvent) that affords defunctionalized SWNTs and two discernable volatile products, the biphenyls 1 and 2, as determined by a GC-MS analysis of the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

[0024] In the following description, specific details are set forth such as specific quantities, sizes, etc. so as to provide a thorough understanding of embodiments of the present invention. However, it will be obvious to those skilled in the art that the present invention may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present invention and are within the skills of persons of ordinary skill in the relevant art.

[0025] Referring to the drawings in general, it will be understood that the illustrations are for the purpose of describing a particular embodiment of the invention and are not intended to limit the invention thereto.

[0026] The present invention is directed towards methods of thermally defunctionalizing functionalized (derivatized) carbon nanotubes (CNTs) in solution or suspended in a liquid medium. Such defunctionalization is largely directed to the removal of sidewall functionality from the CNTs, but can also serve to remove

functionality from the CNT ends. Such methods allow for the resuspension of such defunctionalized CNTs in various solvents and permit the defunctionalization of functionalized CNTs that would normally decompose (or partially decompose) upon thermal treatment. Such methods of defunctionalization can typically lead to defunctionalized CNTs that are essentially pristine (or nearly pristine), and which, in contrast to prior art methods of thermal defunctionalization, can be easily resuspended in a variety of solvents. Additionally, such solvent-based defunctionalization can partially defunctionalize functionalized CNTs in a generally homogeneous manner.

[0027] The methods of the present invention generally comprise the steps of: (a) dissolving or suspending a quantity of functionalized CNTs in a solvent to form a solution/suspension of functionalized CNTs; and (b) heating said solution/suspension to a temperature that will thermally defunctionalize the functionalized CNTs to yield a defunctionalized product.

[0028] CNTs, according to the present invention, include, but are not limited to, single-wall carbon nanotubes (SWNTs), multi-wall carbon nanotubes (MWNTs), double-wall carbon nanotubes (DWNTs), buckytubes, fullerene tubes, tubular fullerenes, graphite fibrils, and combinations thereof. Such CNTs can initially be of a variety and range of lengths, diameters, number of tube walls, chiralities (helicities), etc., and can generally be made by any known technique. The terms "carbon nanotube" and "nanotube" will be used interchangeably herein. Such CNTs are often subjected to one or more purification steps [see, e.g., Chiang et al., *J. Phys. Chem. B*, **2001**, *105*, 1157-1161; Chiang et al., *J. Phys. Chem. B* **2001**, *105*, 8297-8301] and/or methods for separating by length [see, e.g., Farkas et al., *Chemical Physics Letters*, **2002**, *363*, 111-116] and/or electronic type [see, e.g., Chattopadhyay et al., *J. Am. Chem. Soc.*, **2003**, *125*, 3370; Zheng et al., *Science*, **2003**, *302*, 1545-1548; Weisman, *Nat. Mater.*, **2003**, *2*, 569-570; and commonly assigned, co-pending United States Patent Applications Serial Nos. 10/379,022 and 10/379,273, both filed March 4, 2003]. While many of the exemplary embodiments and examples described herein utilize single-wall carbon nanotubes, it should be understood that such methods are generally applicable to all functionalized carbon nanotubes.

[0029] Functionalized CNTs, according to the present invention, can be chemically functionalized derivatives of any of the above-mentioned kinds or types of CNTs. Chemically functionalized, according to the present invention, is the chemical attachment (typically via covalent bonding) of functional moieties to the sidewalls and/or ends of CNTs. Examples of suitably functionalized CNTs include, but are not limited to, those described in the following references: Liu *et al.*, *Science*, **1998**, *280*, 1253-1256; Chen *et al.*, *Science*, **1998**, *282*, 95-98; Holzinger *et al.*, *Angew. Chem. Int. Ed.*, **2001**, *40*, 4002-4005; Khabashesku *et al.*, *Acc. Chem. Res.*, **2002**, *35*, 1087-1095; International Patent Publication Number WO 02/060812, filed January 29, 2002; Bahr *et al.*, *J. Am. Chem. Soc.* **2001**, *123*, 6536-6542; Bahr *et al.*, *Chem. Mater.* **2001**, *13*, 3823-3824; Bahr *et al.*, *J. Mater. Chem.* **2002**, *12*, 1952-1958; Dyke *et al.*, *J. Am. Chem. Soc.*, **2003**, *125*, 1156 -1157; Dyke *et al.*, *Nano Lett.* **2003**, *3*, 1215-1218; Strano *et al.*, *Science*, **2003**, *301*, 1519-1522; Dyke *et al.*, *SynLett* **2004**, 155-160; Dyke *et al.*, *Chem. Eur. J.* **2004**, *10*, 812-817; Ying *et al.*, *Org. Letters*, **2003**, *5*, 1471-1473; Kamaras *et al.*, *Science*, **2003**, *301*, 1501; and Hudson *et al.*, *J. Am. Chem. Soc.* **2004**, *126*, 11158-11159.

[0030] Generally, solvents employed in the methods of the present invention are thermally stable at the temperatures required for defunctionalization of the functionalized CNTs. In some embodiments, the solvent selection is directed by the kinds of functionalized CNTs being defunctionalized. Suitable solvents include, but are not limited to, o-dichlorobenzene (ODCB), benzene, toluene, water, sulfuric acid, oleum (sulfuric acid with dissolved sulfur trioxide), sulfuric acid with dissolved potassium persulfate or other radical initiator such as peroxide, liquid ammonia, liquid ammonia with dissolved alkali metals, alkanes, paraffins, thiophene, and combinations thereof.

[0031] In some embodiments, the functionalized CNTs are further polymer-wrapped and/or surfactant suspended in the solvent or liquid medium prior to being defunctionalized. In these or other embodiments, such polymer wrapping and/or surfactants can serve to keep the CNTs in suspension after they have been completely or partially defunctionalized. See O'Connell *et al.*, *Chem. Phys. Lett.*, **2001**, *342*, 265-271; and O'Connell *et al.*, *Science*, **2002**, *297*, 593-596 for exemplary methods of polymer wrapping and surfactant suspending CNTs, respectively.

[0032] In some embodiments, the solvent includes a polymer such that the defunctionalization is carried out while in a polymer matrix and thereby provides a blended polymer/pristine nanotube sample after defunctionalization and upon removal of the solvent. In some embodiments, the functionalized CNTs are dispersed directly in a polymer matrix, then defunctionalized to yield a product blend comprising unfunctionalized CNTs in a polymer host. Such product blends benefit from the greater dispersability of the functionalized CNTs (relative to unfunctionalized CNTs) in the polymer host.

[0033] The temperatures required for thermal defunctionalization vary depending on the type(s) of functionalized CNTs being defunctionalized. Typically, such defunctionalization temperatures range from about 100°C to about 700°C, and more typically from about 250°C to about 400°C. In some embodiments, a ramped or variable heating process is used.

[0034] Heating a solution or suspension of functionalized CNTs to a temperature required for complete or partial thermal defunctionalization can be accomplished via a variety of heating methods. Suitable heating methods include, but are not limited to, heating mantles, immersion heaters, microwave heating, and combinations thereof.

[0035] In some embodiments, the heating is carried out with stirring, or some other kind of agitation, to ensure homogeneous thermolysis by minimizing thermal gradients within the suspension.

[0036] Typically the thermal defunctionalization process entails a defunctionalization duration, lasting between about 3 minutes and about 2 days, and more typically between about 30 minutes and about 3 hours, during which time the functionalized CNTs are heated.

[0037] In some embodiments, the functionalized CNTs are only partially defunctionalized. This permits product stoichiometries of such partially defunctionalized CNTs that might otherwise not be achievable. In some embodiments, partial defunctionalization is a result of selective thermal defunctionalization according to (n,m) type, with differing types having differing propensities to defunctionalize. In some embodiments, upon being fully or partially defunctionalized, the CNTs flocculate or fall out of suspension/solution.

[0038] In some embodiments, but not all, the defunctionalization is carried out in a sealed reaction vessel. In some embodiments, these sealed reaction vessels permit the use of temperatures that exceed the atmospheric pressure boiling point of the solvent. In some embodiments, some of the defunctionalization products are volatile. In some embodiments, the defunctionalization products react with the suspension/solution medium.

[0039] In some embodiments, one or more analytical techniques are used to evaluate the defunctionalized product and/or byproducts. Such techniques can be used to determine the extent of defunctionalization and the extent to which the defunctionalized carbon nanotubes have been returned to their pristine (original) state. In some embodiments producing volatile defunctionalization products, the liquid defunctionalization medium can be analyzed with gas chromatography-mass spectrometry (GC-MS) or other suitable analytical techniques.

[0040] In some embodiments, the defunctionalized product is only partially defunctionalized, whereas in other embodiments it is completely defunctionalized. The completely defunctionalized CNTs are essentially in their pristine (or nearly pristine) state. An important aspect of the methods described herein is that the defunctionalized CNTs of the present invention (*i.e.*, solvent defunctionalized CNTs) can be redispersed much more easily than CNTs that have been thermally defunctionalized in the dry state.

[0041] In some embodiments, the wholly or partially defunctionalized CNTs of the present invention are redispersed in solvents with the aid of surfactants and/or polymers. In general, such wholly or partially defunctionalized CNTs can be manipulated in essentially any manner in which pristine CNTs can be manipulated.

[0042] Using methods of the present invention, carbon nanotubes (CNTs) chemically modified by bonding (*e.g.*, covalently) functional groups to their sidewalls and/or ends can be thermally defunctionalized in solution, returning the previously functionalized CNTs to their original state. In contrast to thermal defunctionalization processes carried out in the dry state, wherein functionalized CNTs are heated dry in a gaseous or vacuum environment, the present invention does not render the defunctionalized carbon nanotubes unsuspendable/insoluble from that point on. While not intending to be bound by theory, it is believed that solvent-based

defunctionalization methods of the present invention mitigate both the packing of the CNTs into ordered bundles and, possibly, cross-linking which is thought to occur between such functionalized CNTs when they are heated in the dry state.

[0043] The following examples are provided to more fully illustrate some of the embodiments of the present invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute exemplary modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments that are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1

[0044] This Example serves to illustrate how CNTs can be functionalized with diazonium chemistry in accordance with some embodiments of the present invention.

[0045] Referring to FIGURE 1, diazonium species can be generated *in situ* (reaction 1), or added directly (reaction 2), to SWNTs to render them functionalized. Reaction 1 is carried out without any solvent [see Dyke *et al.*, *J. Am. Chem. Soc.*, **2003**, *125*, 1156-1157], and in reaction 2, the SWNTs are first dispersed in water with sodium dodecylsulfate (SDS) [see Dyke *et al.*, *Nano Lett.* **2003**, *3*, 1215-1218]. For a detailed discussion on the mechanistic aspects of such functionalization, see Dyke *et al.*, *SynLett*, **2004**, *1*, 155-160.

[0046] In Examples 2-4 which follow, SWNTs were functionalized with 4-chlorophenylene addends in accordance with reaction 2 in FIGURE 1.

Example 2

[0047] This Example serves to illustrate how functionalized CNTs can be thermally defunctionalized in solution/suspension in accordance with embodiments of the present invention.

[0048] Approximately 0.5 mg of SWNTs (purified HiPco, obtained from Rice University's Carbon Nanotechnology Laboratory), unbundled and functionalized with

4-chlorophenylene addends, were dispersed in 5 mL of *ortho*-dichlorobenzene (ODCB) and placed in a thick-walled, screw-cap tube. The reaction vessel was purged with nitrogen and sealed with a TEFLON cap. The solution was heated in a sand bath placed inside a heating mantle at approximately 450°C with stirring for about 3 hours. After such time, the solution was cooled to room temperature. The regenerated, defunctionalized SWNTs were then filtered through a TEFLON membrane and collected. Defunctionalization was confirmed by absorption and Raman spectroscopies. Subsequent to their defunctionalization, these solvent-defunctionalized SWNTs can be resuspended in any of a number of different solvents (unlike those defunctionalized in the dry state).

Comparative Example 3

[0049] This Example serves to illustrate prior art methods of thermally defunctionalizing functionalized CNTs in the dry state.

[0050] Referring to FIGURE 2, thermogravimetric analysis (TGA) of heavily functionalized (4-chlorophenyl) nanotubes (the same material as used in Example 2) showed 49% weight loss, which corresponds to 1 in 9 carbons on the nanotube bearing an aryl moiety. The addends appear to be removed in two separate thermal regions, one at 200-400°C and a second at 475-550°C. While not intending to be bound by theory, this might be indicative of compressed bands of functionalization vs. dispersed addend regions, or of the defunctionalization temperatures needed for addend expulsion on semiconducting vs. metallic tubes.

[0051] The defunctionalized SWNTs resulting from such thermal defunctionalization in the dry state could not be re-suspended in solvent to any significant extent—even with vigorous agitation.

Example 4

[0052] This Example serves to illustrate how Raman spectroscopy can be used to probe the defunctionalization of functionalized CNTs in both the solvent-based and dry state methods.

[0053] Comparing the Raman spectrum (obtained using 633 nm excitation) of the pristine SWNTs (FIGURE 3A) with that of the 4-chlorophenylene-functionalized material (FIGURE 3B), the characteristic spectroscopic details for covalent

functionalization can be seen [Dyke *et al.*, *SynLett*, 2004, 1, 155-160]. Upon neat thermal treatment in Ar at either 650°C or 450°C for extended periods, the addends can be removed, and the Raman spectra, FIGURES 3C and 3D, respectively, resembled that of the pristine SWNTs shown in FIGURE 3A. However, attempts to disperse these defunctionalized SWNTs in DMF were unsuccessful, even with extended sonication. Using this same heavily functionalized material (0.5 mg), but dissolving it in *ortho*-dichlorobenzene (ODCB, 5 mL) prior to thermal treatment and heating the solution to 450°C for 3 hours in a screw-cap tube (see Example 2) gave defunctionalized material with a corresponding Raman spectrum shown in FIGURE 3E. Raman spectra of this material confirmed significant defunctionalization, albeit not completely pristine-like. However, unlike thermal treatment in the dry state, this protocol yields material with solubility that is better than that of material obtained by thermally defunctionalizing in the dry state.

Example 5

[0054] This Examples serves to illustrate how byproducts from some of the solvent-based defunctionalization method of the present invention can be analyzed.

[0055] While not intending to be bound by theory, and as discussed generally above, the thermal treatment of functionalized CNT material while dispersed in a solvent such as ODCB possibly prevents nanotube radicals from combining to form nanotube dimers; instead, two radicals on the same nanotube might combine by extended conjugation to regenerate the C—C double-bond. Conversely, extensive rebundling might be minimized under such solvent-based conditions. To gain further insight into such solvent-based thermal defunctionalization, the byproducts of a ODCB-thermalized reaction of 4-*tert*-butylphenyl functionalized SWNTs were examined by GC-MS analysis of the ODCB solution. Referring to FIGURE 4, two biphenyls, 1 and 2, were generated by the addends coupling with the solvent, which substantiates (a) the *tert*-butylphenyl attachment to the nanotube and (b) the reactive nature of the moiety as it is evolved from the nanotube. Interestingly, there was no discernible di(*tert*-butyl)biphenyl present in the reaction mixture, so the addends did not evolve in pairs. If the addends had evolved as aryl anions, reaction with solvent would likely have led to chloride substitution on the ODCB. Expulsion as the cation would have led to a highly reactive species that could afford the products observed

in FIGURE 4. However, thermolytic cleavage most likely proceeds via a homolytic process.

[0056] All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.